

29  
1. A crystal growth method for adding or crystallizing nitrogen in a crystal, comprising

5  
a step of supplying aluminum and ammonium (NH<sub>3</sub>) to a surface of the crystal,

wherein addition or crystallization of the nitrogen from the ammonium which is supplied to the surface of the crystal into the surface of the crystal is accelerated by the aluminum supplied to the surface of the crystal.

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30  
2. A crystal growth method according to claim 1, wherein decomposition of ammonium and adsorption of nitrogen on a crystal surface is accelerated by aluminum.

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31  
3. A crystal growth method according to claim 1, wherein the aluminum exists at least in an outermost surface of a growing layer.

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32  
4. A crystal growth method according to claim 1, wherein an amount of nitrogen added to a crystal, a nitrogen composition, an amount of nitrogen adsorbed on a crystal surface and an amount of an element in the crystal surface

which is substituted with a nitrogen atom are controlled based on an amount or composition ratio of added aluminum.

33  
3. A crystal growth method according to claim 1, wherein  
5 aluminum is added to or crystallized in a restricted region, whereby only in the restricted region, nitrogen is added or crystallized, a nitrogen atom is adsorbed, or an element in a crystal surface is substituted with a nitrogen atom.

10  
34  
3. A crystal growth method according to claim 1, wherein  
a method selected from among a molecular beam epitaxial (MBE) growth method, a metal organic molecular beam epitaxial (MO-MBE) growth method, a gas source molecular beam epitaxial (GS-MBE) growth method, and a chemical beam epitaxial (CBE) growth method is used.

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35  
3. A crystal growth method according to claim 1, wherein crystal growth of a III-V compound semiconductor including, as V group components, nitrogen and a V group element other than nitrogen is performed.

36  
3. A crystal growth method according to claim 35, wherein  
at least one of arsenic (As), phosphorus (P), and

antimony (Sb) is selected as the V group element other than nitrogen.

37  
9. A crystal growth method according to claim <sup>35</sup>~~7~~, wherein  
5 a substrate temperature is in a range from 450°C to 640°C.

14  
10. A crystal growth method according to claim 1, wherein  
a surface of single crystal substrate is a crystal surface  
slanted from a (100) surface in a [011] direction  
10 (A direction) or a crystal face which is equivalent in  
a crystallographic sense to the slanted crystal surface.

39  
11. A crystal growth method according to claim <sup>38</sup>~~10~~,  
wherein the slant angle is within a range equal to 2° or  
15 more and equal to 25° or less.

40  
12. A crystal growth method according to claim 1, wherein  
one or more pairs of semiconductor layer A and  
semiconductor layer B are superposed, the semiconductor  
20 layer A including at least aluminum and nitrogen in its  
composition but not including indium in its composition,  
and the semiconductor layer B including at least indium  
in its composition but not including nitrogen in its  
composition.

41  
13. A crystal growth method according to claim 12,  
wherein the thickness of each of the semiconductor  
layers A and B is one molecular layer or more, and ten  
molecular layers or less.

42  
14. A crystal growth method according to claim 1, wherein  
crystal growth is performed by applying a source material  
to a substrate in a crystal growth room which is evacuated  
of air, and a mean free path of a molecule of each source  
material is longer than a distance between the substrate  
and a source of the source material.

43  
15. A crystal growth method according to claim 1, wherein  
ammonium in the form of gas is used as a nitrogen source  
material, and a source material of another element is  
obtained by evaporating a solid of a single element.

44  
16. A crystal growth method according to claim 1, wherein  
ammonium in an undecomposed state is supplied as a  
nitrogen source material and decomposed on a surface of  
the substrate.

<sup>45</sup>  
~~17~~. A crystal growth method according to claim 1, wherein crystal growth is performed over an underlying (substrate) crystal which does not include nitrogen as a principal element.

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<sup>46</sup>  
~~18~~. A crystal growth method according to claim <sup>45</sup>~~17~~, wherein the underlying (substrate) crystal is selected from GaAs, InP, GaP, GaSb, and Si.

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<sup>47</sup>  
~~19~~. A semiconductor device comprising a semiconductor layer formed by the crystal growth method of claim 1.

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<sup>48</sup>  
~~20~~. A semiconductor device according to claim <sup>47</sup>~~19~~, wherein the semiconductor device is a light emitting element, and the semiconductor layer forms a light emitting layer thereof.

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<sup>49</sup>  
~~21~~. A semiconductor device comprising a semiconductor layer formed by the crystal growth method of claim <sup>38</sup>~~10~~.

<sup>50</sup>  
~~22~~. A semiconductor device according to claim <sup>49</sup>~~21~~, wherein the semiconductor device is a light emitting element, and the semiconductor layer forms a light emitting layer thereof.

<sup>51</sup>  
23. A semiconductor device comprising a semiconductor layer formed by the crystal growth method of claim <sup>40</sup> 12.

5 <sup>52</sup>  
24. A semiconductor device according to claim <sup>51</sup> 23, wherein the semiconductor device is a light emitting element, and the semiconductor layer forms a light emitting layer thereof.

10 <sup>53</sup>  
25. A system which uses the semiconductor device of claim <sup>41</sup> 19.

15 <sup>54</sup>  
26. A system which uses the semiconductor device of claim <sup>49</sup> 21.

<sup>55</sup>  
27. A semiconductor device comprising a semiconductor layer formed by the crystal growth method of claim <sup>42</sup> 14.

20 <sup>56</sup>  
28. A semiconductor device according to claim <sup>55</sup> 27, wherein the semiconductor device is a light emitting element, and the semiconductor layer forms a light emitting layer thereof.

<sup>57</sup>  
~~29~~. A semiconductor device comprising a semiconductor layer formed by the crystal growth method of claim <sup>43</sup>~~15~~.

<sup>54</sup>  
~~30~~. A semiconductor device according to claim <sup>57</sup>~~29~~, wherein  
5 the semiconductor device is a light emitting element, and  
the semiconductor layer forms a light emitting layer  
thereof.

*As cont*  
<sup>59</sup>  
~~31~~. A semiconductor device comprising a semiconductor layer formed by the crystal growth method of claim <sup>44</sup>~~16~~.  
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<sup>60</sup>  
~~32~~. A semiconductor device according to claim <sup>59</sup>~~31~~, wherein  
the semiconductor device is a light emitting element, and  
the semiconductor layer forms a light emitting layer  
15 thereof.

<sup>61</sup>  
~~33~~. A semiconductor device comprising a semiconductor layer formed by the crystal growth method of claim <sup>45</sup>~~17~~.

<sup>62</sup>  
~~34~~. A semiconductor device according to claim <sup>61</sup>~~33~~, wherein  
20 the semiconductor device is a light emitting element, and  
the semiconductor layer forms a light emitting layer  
thereof.

<sup>63</sup>  
35. A crystal growth method for adsorbing a nitrogen atom on a surface of a crystal, the crystal including aluminum in the surface thereof, comprising steps of:

growing the crystal including the aluminum on the  
5 surface; and

supplying ammonium ( $\text{NH}_3$ ) to the surface of the crystal including the aluminum in the surface thereof,

*Ammonia*  
wherein adsorption of the nitrogen atom generated by decomposition of the ammonium supplied to the surface  
10 of the crystal is accelerated by the aluminum included in the surface of the crystal.

<sup>64</sup>  
36. A crystal growth method according to claim <sup>63</sup>~~35~~,  
wherein decomposition of ammonium and adsorption of  
15 nitrogen on a crystal surface is accelerated by aluminum.

<sup>65</sup>  
37. A crystal growth method according to claim <sup>63</sup>~~35~~,  
wherein the aluminum exists at least in an outermost  
surface of a growing layer.

20 <sup>66</sup>  
38. A crystal growth method according to claim <sup>63</sup>~~35~~,  
wherein an amount of nitrogen added to a crystal, a nitrogen composition, an amount of nitrogen adsorbed on a crystal surface and an amount of an element in the crystal



surface which is substituted with nitrogen are controlled based on an amount or composition ratio of added aluminum.

*67*  
39. A crystal growth method according to claim *63*  
5 wherein aluminum is added to or crystallized in a re-  
stricted region, whereby only in the restricted region,  
nitrogen is added or crystallized, a nitrogen atom is  
adsorbed, or an element in a crystal surface is  
substituted with a nitrogen atom.

*68*  
40. A crystal growth method according to claim *63*  
10 wherein a method selected from among a molecular beam  
epitaxial (MBE) growth method, a metal organic molecular  
beam epitaxial (MO-MBE) growth method, a gas source  
15 molecular beam epitaxial (GS-MBE) growth method, and a  
chemical beam epitaxial (CBE) growth method is used.

*69*  
41. A crystal growth method according to claim *63*  
20 wherein crystal growth of a III-V compound semiconductor  
including, as V group components, nitrogen and a V group  
element other than nitrogen is performed.

*70*  
42. A crystal growth method according to claim *69*  
wherein at least one of arsenic (As), phosphorus (P), and

antimony (Sb) is selected as the V group element other than nitrogen.

<sup>71</sup>  
43. A crystal growth method according to claim <sup>69</sup>41,  
5 wherein a substrate temperature is in a range from 450°C to 640°C.

<sup>72</sup>  
44. A crystal growth method according to claim <sup>63</sup>35,  
comprising a series of steps including at least steps of:  
10 supplying a III group source material including aluminum of less than one atomic layer;  
subsequently, supplying ammonium so as to adsorb nitrogen atoms of less than one atomic layer; and  
supplying a source material of a V group element  
15 other than nitrogen,  
wherein the series of steps are repeated one time or more.

<sup>73</sup>  
45. A crystal growth method according to claim <sup>72</sup>44,  
20 wherein in the step of supplying ammonium so as to adsorb nitrogen of less than one atomic layer, the source material of the V group element other than nitrogen is not supplied at the same time.

<sup>74</sup>  
~~46~~. A crystal growth method according to claim <sup>72</sup>~~44~~,  
wherein crystal growth is performed over a single crystal  
substrate in which a {100} surface is a principal plane.

5 <sup>75</sup>  
~~47~~. A crystal growth method according to claim <sup>74</sup>~~46~~,  
wherein a surface of the single crystal substrate is a  
crystal surface slanted from a (100) surface in a  
[011] direction (A direction) or a crystal face which is  
equivalent in a crystallographic sense to the slanted  
10 crystal surface.

<sup>76</sup>  
~~48~~. A crystal growth method according to claim <sup>75</sup>~~47~~,  
wherein the slant angle is within a range equal to 2° or  
more and equal to 25° or less.

15 <sup>77</sup>  
~~49~~. A crystal growth method according to claim <sup>63</sup>~~35~~,  
wherein one or more pairs of semiconductor layer A and  
semiconductor layer B are superposed, the semiconductor  
layer A including at least aluminum and nitrogen in its  
20 composition but not including indium in its composition,  
and the semiconductor layer B including at least indium  
in its composition but not including nitrogen in its  
composition.

44-49  
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<sup>78</sup>  
50. A crystal growth method according to claim <sup>77</sup>~~49~~,  
wherein the thickness of each of the semiconductor  
layers A and B is one molecular layer or more, and ten  
molecular layers or less.

5

<sup>79</sup>  
51. A crystal growth method according to claim <sup>63</sup>~~35~~,  
wherein crystal growth is performed by applying a source  
material to a substrate in a crystal growth room which  
is evacuated of air, and a mean free path of a molecule  
of each source material is longer than a distance between  
the substrate and a source of the source material.

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<sup>80</sup>  
52. A crystal growth method according to claim <sup>63</sup>~~35~~,  
wherein ammonium in the form of gas is used as a nitrogen  
source material, and a source material of another element  
is obtained by evaporating a solid of a single element.

15

<sup>81</sup>  
53. A crystal growth method according to claim <sup>63</sup>~~35~~,  
wherein ammonium in an undecomposed state is supplied as  
a nitrogen source material and decomposed on a surface  
of the substrate.

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<sup>82</sup>  
54. A crystal growth method according to claim <sup>63</sup>~~35~~,  
wherein crystal growth is performed over an underlying

(substrate) crystal which does not include nitrogen as a principal element.

- 83  
55. A crystal growth method according to claim <sup>82</sup>54,  
5 wherein the underlying (substrate) crystal is selected from GaAs, InP, GaP, GaSb, and Si.

- At cont*  
84  
56. A semiconductor device comprising a semiconductor layer formed by the crystal growth method of claim <sup>63</sup>55.

- 10 85  
57. A semiconductor device according to claim <sup>84</sup>56, wherein the semiconductor device is a light emitting element, and the semiconductor layer forms a light emitting layer thereof.

- 15 86  
58. A semiconductor device comprising a semiconductor layer formed by the crystal growth method of claim <sup>75</sup>57.

- 20 87  
59. A semiconductor device according to claim <sup>86</sup>58, wherein the semiconductor device is a light emitting element, and the semiconductor layer forms a light emitting layer thereof.

<sup>89</sup>  
~~61~~. A semiconductor device according to claim <sup>88</sup>~~60~~, wherein the semiconductor device is a light emitting element, and the semiconductor layer forms a light emitting layer thereof.

91  
63. A system which uses the semiconductor device of  
88  
claim 60.

93  
65. A semiconductor device according to claim 64, wherein the semiconductor device is a light emitting element, and the semiconductor layer forms a light emitting layer thereof.

94  
66. A semiconductor device comprising a semiconductor layer formed by the crystal growth method of claim 52.

95  
67. A semiconductor device according to claim 94, wherein  
the semiconductor device is a light emitting element, and  
the semiconductor layer forms a light emitting layer  
5 thereof.

96  
68. A semiconductor device comprising a semiconductor  
layer formed by the crystal growth method of claim 81.  
97  
10 69. A semiconductor device according to claim 96, wherein  
the semiconductor device is a light emitting element, and  
the semiconductor layer forms a light emitting layer  
thereof.

98  
15 70. A semiconductor device comprising a semiconductor  
layer formed by the crystal growth method of claim 82.  
99

71. A semiconductor device according to claim 98, wherein  
the semiconductor device is a light emitting element, and  
20 the semiconductor layer forms a light emitting layer  
thereof.

~~100~~  
~~72. A crystal growth method for substituting a portion  
of elements included in a crystal surface with nitrogen~~

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atoms, the surface of the crystal further including aluminum, comprising steps of:

growing the crystal; and

supplying ammonium ( $\text{NH}_3$ ) to the surface of the crystal,

wherein substitution of the portion of the elements with the nitrogen atom from the ammonium supplied to the surface of the crystal is accelerated by the aluminum included in the surface of the crystal.

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<sup>101</sup>  
73. A crystal growth method according to claim <sup>100</sup>72, wherein decomposition of ammonium and adsorption of nitrogen on a crystal surface is accelerated by aluminum.

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<sup>102</sup>  
74. A crystal growth method according to claim <sup>100</sup>72, wherein the aluminum exists at least in an outermost surface of a growing layer.

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<sup>103</sup>  
75. A crystal growth method according to claim <sup>100</sup>72, wherein an amount of nitrogen added to a crystal, a nitrogen composition, an amount of nitrogen adsorbed on a crystal surface and an amount of an element in the crystal surface which is substituted with nitrogen are controlled based on an amount or composition ratio of added aluminum.



*104*  
76. A crystal growth method according to claim *72*,  
wherein aluminum is added to or crystallized in a re-  
stricted region, whereby only in the restricted region,  
5 nitrogen is added or crystallized, a nitrogen atom is  
adsorbed, or an element in a crystal surface is  
substituted with a nitrogen atom.

*105*  
77. A crystal growth method according to claim *72*,  
10 wherein a method selected from among a molecular beam  
epitaxial (MBE) growth method, a metal organic molecular  
beam epitaxial (MO-MBE) growth method, a gas source  
molecular beam epitaxial (GS-MBE) growth method, and a  
chemical beam epitaxial (CBE) growth method is used.

*106*  
78. A crystal growth method according to claim *72*,  
15 wherein crystal growth of a III-V compound semiconductor  
including, as V group components, nitrogen and a V group  
element other than nitrogen is performed.

*107*  
79. A crystal growth method according to claim *78*,  
20 wherein at least one of arsenic (As), phosphorus (P), and  
antimony (Sb) is selected as the V group element other  
than nitrogen.

<sup>108</sup>  
~~80~~. A crystal growth method according to claim <sup>106</sup>78,  
wherein a substrate temperature is in a range from 450°C  
to 640°C.

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<sup>109</sup>  
~~81~~. A crystal growth method according to claim <sup>100</sup>72,  
comprising a series of steps including at least steps of:  
forming a III-V compound crystal layer including at least  
one molecular layer of aluminum; and subsequently,  
10 supplying ammonium so as to substitute a portion of  
V group atoms in the III-V compound crystal layer with  
nitrogen atoms, wherein the series of steps are repeated  
one time or more.

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<sup>110</sup>  
~~82~~. A crystal growth method according to claim <sup>100</sup>72,  
comprising at least steps of:

crystal-forming a layered structure including at  
least a first semiconductor layer containing aluminum and  
a second semiconductor layer superposed thereon;

20

etching the layered structure while masking a  
portion of the layered structure such that the first  
semiconductor layer is exposed in a portion of an etched  
surface; and

supplying ammonium to the etched surface while

Al cont

heating the layered structure such that at least a portion of a constituent element in the first semiconductor layer is substituted with nitrogen.

5 <sup>111</sup>  
~~83.~~ A crystal growth method according to claim <sup>110</sup> ~~82~~,  
wherein the etched surface is a (n11)A surface (n=1, 2,  
3, ...).

10 <sup>112</sup>  
84. A crystal growth method according to claim <sup>100</sup> ~~72~~,  
wherein a surface of single crystal substrate is a crystal  
surface slanted from a (100) surface in a [011] direction  
(A direction) or a crystal face which is equivalent in  
a crystallographic sense to the slanted crystal surface.

15 <sup>113</sup>  
85. A crystal growth method according to claim <sup>112</sup> ~~84~~,  
wherein the slant angle is within a range equal to 2° or  
more and equal to 25° or less.

20 <sup>114</sup>  
86. A crystal growth method according to claim <sup>100</sup> ~~72~~,  
wherein one or more pairs of semiconductor layer A and  
semiconductor layer B are superposed, the semiconductor  
layer A including at least aluminum and nitrogen in its  
composition but not including indium in its composition,  
and the semiconductor layer B including at least indium

in its composition but not including nitrogen in its composition.

*115*  
~~87.~~ A crystal growth method according to claim *114* ~~86~~,  
wherein the thickness of each of the semiconductor  
layers A and B is one molecular layer or more, and ten  
molecular layers or less.

*116*  
10 88. A crystal growth method according to claim *100* ~~72~~,  
wherein crystal growth is performed by applying a source  
material to a substrate in a crystal growth room which  
is evacuated of air, and a mean free path of a molecule  
of each source material is longer than a distance between  
the substrate and a source of the source material.

*117*  
15 89. A crystal growth method according to claim *100* ~~72~~,  
wherein ammonium in the form of gas is used as a nitrogen  
source material, and a source material of another element  
is obtained by evaporating a solid of a single element.

*118*  
20 90. A crystal growth method according to claim *100* ~~72~~,  
wherein ammonium in an undecomposed state is supplied as  
a nitrogen source material and decomposed on a surface  
of the substrate.

119  
91. A crystal growth method according to claim <sup>100</sup>72,  
wherein crystal growth is performed over an underlying  
(substrate) crystal which does not include nitrogen as  
5 a principal element.

*A, cont*  
<sup>120</sup>92. A crystal growth method according to claim <sup>119</sup>91,  
wherein the underlying (substrate) crystal is selected  
from GaAs, InP, GaP, GaSb, and Si.

10  
<sup>121</sup>93. A semiconductor device comprising a semiconductor  
layer formed by the crystal growth method of claim <sup>100</sup>72.

<sup>122</sup>94. A semiconductor device according to claim <sup>121</sup>93, wherein  
15 the semiconductor device is a light emitting element, and  
the semiconductor layer forms a light emitting layer  
thereof.

<sup>123</sup>95. A semiconductor device comprising a semiconductor  
20 layer formed by the crystal growth method of claim <sup>112</sup>84.

<sup>124</sup>96. A semiconductor device according to claim <sup>123</sup>95, wherein  
the semiconductor device is a light emitting element, and  
the semiconductor layer forms a light emitting layer

thereof.

<sup>125</sup>  
97. A semiconductor device comprising a semiconductor layer formed by the crystal growth method of claim <sup>114</sup>86.

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<sup>126</sup>  
98. A semiconductor device according to claim <sup>125</sup>97, wherein the semiconductor device is a light emitting element, and the semiconductor layer forms a light emitting layer thereof.

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<sup>127</sup>  
99. A method for forming a semiconductor microwire structure wherein:

the crystal growth method of claim <sup>110</sup>82 is used when forming a semiconductor microstructure having a periodically-positioned wire pattern;

15

a diffraction grating is formed by the step of etching the layered structure while masking a portion of the layered structure such that the first semiconductor layer is exposed in a portion of an etched surface; and

20

a periodical wire structure is formed at a 1/2 of the pitch of the diffraction grating by the step of supplying ammonium to the etched surface while heating the layered structure such that at least a portion of a constituent element in the first semiconductor layer is

substituted with nitrogen.

- 128*  
100. A method for forming a semiconductor microwire structure according to claim <sup>127</sup>99, wherein the wire structure is an absorptive diffraction grating section of a gain-coupled distributed feedback semiconductor laser having an absorptive diffraction grating, or a quantum wire.
- 129*  
101. A method for forming a semiconductor microwire structure according to claim <sup>127</sup>99, wherein ammonium in an undecomposed state is supplied as a nitrogen source material and decomposed on a surface of the substrate.
- 130*  
102. A method for forming a semiconductor microwire structure according to claim <sup>127</sup>99, wherein crystal growth is performed over an underlying (substrate) crystal which does not include nitrogen as a principal element.
- 131*  
103. A method for forming a semiconductor microwire structure according to claim <sup>130</sup>102, wherein the underlying (substrate) crystal is selected from GaAs, InP, GaP, GaSb, and Si.

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<sup>138</sup>  
110. A semiconductor device comprising a semiconductor  
layer formed by the crystal growth method of claim <sup>118</sup>90.



*139*  
~~111~~. A semiconductor device according to claim ~~110~~,<sup>138</sup>  
wherein the semiconductor device is a light emitting  
element, and the semiconductor layer forms a light  
emitting layer thereof.

5

*140*  
~~112~~. A semiconductor device comprising a semiconductor  
layer formed by the crystal growth method of claim ~~91~~.<sup>119</sup>

10

*141*  
~~113~~. A semiconductor device according to claim ~~112~~,<sup>140</sup>  
wherein the semiconductor device is a light emitting  
element, and the semiconductor layer forms a light  
emitting layer thereof.